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**No. 26.—The Compensation Method of
determining the F° of Oxidation
of Hydrogen Iodide.**

BY
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**THE COMPENSATION METHOD OF DE-
TERMINING THE RATE OF OXIDA-
TION OF HYDROGEN IODIDE**

By JAMES M. BELL

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THE COMPENSATION METHOD OF DETERMINING THE RATE OF OXIDATION OF HYDROGEN IODIDE

BY JAMES M. BELL

Among the earliest researches on the rate of progress of a chemical reaction is that of Messrs. Harcourt and Esson, "On the Oxidation of Hydrogen Iodide by Hydrogen Peroxide."¹ This paper is important, not only because it is one of the very first successful attempts to formulate the relation between the rate of a chemical reaction and the concentration of the reacting substances, but because the method of measurement introduced by the authors has since been employed in many similar researches. The method in question, which, borrowing a word from Schükarew, I propose to call the "Compensation Method," is described in the section following.

Owing to discrepancies between the results of certain rate measurements carried out by means of the Compensation Method, and others in which more direct methods were employed, I was led to enquire into the conditions under which the former method is applicable. The present paper contains the results of this examination, a résumé of the various cases in which the Compensation Method has been employed heretofore, and three series of experiments to test its applicability when hydrogen peroxide, chloric acid, and chromic acid, respectively, are the oxidizing agents.

The Compensation Method

Harcourt and Esson's method of working "consisted in the addition to a solution containing hydrogen dioxide, hydrogen iodide, and a little starch, of successive portions of sodium hyposulphite. Not only is the iodine which may have been formed in the solution instantly converted into iodide by this reagent, but the iodine which is continually being liberated is at once

¹ Jour. Chem. Soc. 20, 476 (1867).

combined, so that the liquid, though it contain starch, and though iodine is being formed in it, rests quite colourless, as long as any hyposulphite remains. But when the last trace of hyposulphite has been changed into tetrathionate by the action of the iodine, the portion of iodine next formed remains free, and the liquid suddenly becomes blue. The addition of another small portion of hyposulphite again removes the colour; till all the hyposulphite has been destroyed, it remains colourless, and then the blue color reappears."

The ratio between the amount of each "small portion" of thiosulphate of soda and the time which elapsed before the blue colour appeared was regarded as measuring the rate of oxidation of the hydriodic acid by hydrogen peroxide; and the thiosulphate was supposed to act only as a "compensator", by means of which the passage of the reaction through a given point—adjusted by altering the amount of thiosulphate—could be detected.

Conditions of applicability

It is obvious that the intervals between the reappearances of the blue color in Harcourt and Esson's experiments only measured the time necessary for the destruction of the thiosulphate in the reacting mixture; the authors' interpretation is based on the assumptions, (1) that the thiosulphate reacts only with the iodine liberated by the action of the oxidizing agent on the hydriodic acid, and (2) that its presence in no way influences the course of that action. The truth of these assumptions can be proved only by a special investigation, *which must be repeated with each oxidizing agent*. This point, which was apparently quite clear to Harcourt and Esson, seems to have been overlooked by the chemists who subsequently employed the Compensation Method.

In a solution containing acid, an oxidizing agent, and an iodide, sodium thiosulphate may enter into reaction in one or more of the following ways:—

¹ Loc. cit. page 476.

(I) It may be converted into tetrathionat. by the iodine liberated from the iodide by the oxidizing agent.

(II) It may be converted into sulphite, etc., by the action of the acid.

(III) It may be oxidized by the direct action of the oxidizing agent.

Moreover,

(IV) The rate of oxidation of the iodide may be affected by the presence of the thiosulphate or of its oxidation products, and similarly,

(V) The rates at which reactions (II) and (III) take place may be modified (catalyze!) by the presence of the oxidizing agent, the iodide, or the products of the reactions themselves.

The rate of the reaction between thiosulphate and acid has been studied by v. Oettingen.¹ It depends upon the concentration of the acid and may be reduced by diminishing the latter. With acids of the concentrations employed by the authors enumerated in the succeeding paragraph, the rate of this reaction is very slow. This is doubly fortunate, for not only would the sulphite react with the iodine, but as will be shown in the experimental part, it may cause a remarkable acceleration of the reaction between the thiosulphate and the oxidizing agent. The rate of oxidation of the thiosulphate, on the other hand, has been very little studied (a few measurements are contained in the present paper), and nothing has been published as to the magnitude or sign of the catalytic actions enumerated under (IV) and (V).

The Compensation Method is applicable only to cases where the amounts of thiosulphate entering into reactions (II) and (III) are negligible in comparison with that entering into reaction (I), and where the catalytic influences enumerated in (IV) are non-existent. If these conditions are fulfilled, the results of the experiments will be unaffected by the concentration of the thiosulphate in the reacting mixture, i. e., by the amount

¹ Zeit. phys. Chem. 33, 1 (1900).

of each "small portion" added: whereas it is obvious that if the thiosulphate enters into direct reaction with any of the constituents of the solution (the acid, or the oxidizing agent, for instance), or if it accelerates the reaction whose rate is supposed to be measured, an increase in the amount of each small portion will increase the apparent rate.

The last consideration suggests an easy test of the *inapplicability* of the compensation method to any particular case; but it is only by comparison of the results of the method in question with those obtained in the absence of thiosulphate, that evidence of its applicability can be obtained. In making the comparison, allowance must obviously be made for the possible effect of iodine accumulated in the solution.

Cases in which the Compensation Method has been employed

Harcourt and Esson. — "*On the Oxidation of Hydrogen Iodide by Hydrogen Peroxide.*"¹ The authors assured themselves that "in a dilute solution containing iodide, hyposulphite is neither decomposed into sulphur and sulphite by the action of hydrogen sulphate or chloride, nor is it oxidized, or in any way acted on directly by hydrogen dioxide."

Pendlebury and Seward. — "*An Investigation on the Interaction of Hydrogen Chloride and Chlorate in the Presence of Potassium Iodide.*"² Apparently no endeavor was made to check the results by the use of different amounts of thiosulphate, or by comparison with those furnished by other methods of analysis. The whole matter is dismissed with the words, "the intervals date from one appearance of the color to the next appearance, and as the rate is not affected by the presence of a small amount of iodine or a small diminution in the amount of iodide, it is clear that the fact of the addition and admixture of the thiosulphate, not following immediately on the appearance of the blue color, does not disturb the uniformity of the rate change."

Judson and Walker. — "*Reduction of Bromic Acid; and*

¹ Jour. Chem. Soc. 20, 476 (1867).

² Proc. Roy. Soc. 45, 396 (1889).

the Law of Mass Action."¹ In their first series of experiments, the authors added thiosulphate to the reacting mixture, and noted the time at which the yellow color of free bromine appeared in the solution. Finding, however, that the time which elapsed before the yellow color appeared was much shorter when the thiosulphate was added *in toto* at the beginning of the experiment, than when the same quantity was added in small portions as the reaction proceeded, they abandoned the Compensation Method and adopted the "more tedious and less accurate method" of titration at measured intervals of time.

Schükarew.—"*Über polymolekulare Umwandlungen.*"² The author employed the Compensation Method to measure the rates of oxidation of various iodides by ferric salts, chromic acid, and nitrous acid. The results are not checked by the use of an independent method, but the author assured himself that under the conditions of his experiments "the time was proportional to the quantity of thiosulphate employed", that is, that changing the concentration of the thiosulphate did not affect the rate.

With regard to direct action between the oxidizing agent and thiosulphate, Schükarew says—"One might think that the thiosulphate would react directly with the ferric chloride. This is possible;³ it is still more probable that the thiosulphate acts merely as an accelerator. * * * In the first case we have a simple method of calculation by means of which this secondary reaction is eliminated, while for the purposes of this paper the acceleration is of no moment."

The "simple method of calculation" is based upon the assumption that the two reactions (*viz.*, oxidation of the thiosulphate, and oxidation of the iodide) take place independently in the solution, so that the rate of the former is not affected by the concentration of the iodide. In the next section I have de-

¹ Jour. Chem. Soc. 73, 410 (1898).

² Zeit. phys. Chem. 38, 353 (1901).

³ Sodium thiosulphate is oxidized by ferric chloride so rapidly that it has been proposed (by Scheerer, in 1859) to employ a solution of sodium thiosulphate for the volumetric determination of iron. F. Mohr's *Titrimethode*, 7th ed., p. 355.

veloped the mathematical consequences of this assumption; as will be shown in the experimental part, they are not in accordance with the observations.

To recapitulate: the Compensation Method has been employed in measuring the rate of oxidation of hydriodic acid by hydrogen peroxide, chloric acid, ferric salts, chromic acid, and nitrous acid. In no case have the results been checked by the use of an independent method. Except in the case of hydrogen peroxide, the direct action of the oxidizing agent on the thiosulphate has not been studied; and the attempt which one author has made to eliminate the effect of this direct action by calculation, is based on erroneous assumptions.

Development of the theory of the Compensation Method, allowing for direct oxidation

The equations of this section are obtained by assuming that in a solution containing a thiosulphate, an iodide, and an oxidizing agent, the thiosulphate is simultaneously acted on by the oxidizing agent, and by the iodine set free by the oxidation of the iodide. The action of the acid on the thiosulphate is neglected, and no account is taken of catalytic actions. In other words, of the five possibilities enumerated on page 63, the first and second are admitted, and the other three rejected. It is further assumed, that the oxidizing agent is present in a large quantity as compared with the thiosulphate; so that the concentration of the former remains sensibly constant during the reaction; the concentration of the iodide remains, of course, absolutely so. Lastly, in accordance with experiments described later, the rate of oxidation of the thiosulphate is set proportional to the first power of its own concentration. It would be an easy matter to introduce the second or a higher power if occasion should arise.

As the reaction between iodine and thiosulphate is instantaneous, and as (under the assumptions enumerated above) the rate of oxidation of the iodide is constant, the rate of loss of thiosulphate due to reaction (I) p. 63 must be constant also, or

$$\partial x / \partial t = k_0,$$

where the value of k_0 depends on the temperature, and on the concentration of the iodide and of the oxidizing agent.

Integrating, with the condition that $x = 0$ when $t = 0$ and setting $x = A$ (the initial concentration of the thiosulphate) we obtain

$$T_0 = k_0 A \quad (1)$$

the time in which the thiosulphate would be totally destroyed by the operation of reaction (I) alone.

The rate of loss of thiosulphate due to direct oxidation is represented by the equation

$$x/t = k_1(A - x),$$

(A being the initial concentration of the thiosulphate, as before) and the total loss due to both causes combined, by

$$dx/dt = k_0 + k_1(A - x).$$

Integrating, under the same condition as before, and introducing the abbreviation $k = k_0/k_1$, this becomes

$$k_1 t = \log. \text{nat.} \{ (A + k)/(A + k - x) \}, \quad (2)$$

whence the time T , at which the solution turns blue, viz: when $x = A$.

$$T = (1/k_1) \log. \text{nat.} (1 + A/k). \quad (3)$$

The following table gives the values of T_0 in seconds calculated from equations (1) and (3) for three values of T and five of k_1 ; under E are entered the percentage errors introduced by confounding T with T_0 , that is, by neglecting the effect of the direct action of the oxidizing agent on the thiosulphate. Other circumstances equal, the error decreases with decrease in T ; in practice, however, it is not possible to obtain accurate results when T is less than 20 seconds.

TABLE I.

k_1	$T = 20$			$T = 40$			$T = 60$		
	T_0	E Percent		T_0	E Percent		T_0	E Percent	
0.001	20.2	1		40.7	2		61.8	3	
0.005	21.04	5		44.3	11		70.0	17	
0.010	22.15	11		49.2	23		82.2	37	
0.020	24.59	23		61.3	53		116.0	83	
0.050	34.36	72		127.8	219		382.0	536	

For values of A/k not greater than 1.3, equation (2) may be replaced by the following with an error of less than three percent :

$$k_1 T = A/k - (1/2)(A/k)^2,$$

whence

$$T/A = 1/k_0 - (1/2)Ak_1/k_0^2. \quad (4)$$

That is to say, if T be determined for different values of A , and the results be plotted with A and T/A as coordinates, the points should lie on a straight line, which is parallel to the A axis if $k_1 = 0$, and whose inclination increases with increase in the ratio k_1/k_0 .

I. HYDROGEN PEROXIDE AS OXIDIZING AGENT

The following experiment were carried out (under the same conditions of concentration and temperature as those of Messrs. Harcourt and Esson) to ascertain whether the ratio T/A is independent of A , whether sodium thiosulphate is oxidized by hydrogen peroxide, and whether the results of the Compensation Method are identical with those obtained in the absence of thio-sulphate.

Solutions

As comparative results, only, were wanted, the compositions of the solutions were not determined with any great accuracy. The stock solutions were:—

Acid: sulphuric, approximately 8 times normal.

Iodide: 30 grammes potassium iodide per liter.

Thiosulphate: 4 grammes cryst. sodium thiosulphate per liter.

Iodine: one volume of the thiosulphate solution was equivalent to approximately five volumes of the iodine solution.

Peroxide: 0.75 gramme sodium peroxide per liter. A direct experiment showed that the amount of iodine liberated by the action of hydriodic acid in excess on 10 cc of the peroxide solution, was equivalent to 7.35 cc of the thiosulphate solution.

Results of the measurements — Series A

In each of the following five experiments, one liter of an "oxidizing mixture" was used, containing water, 100 cc acid, 10 cc peroxide, and 5 cc of a dilute starch solution. The experiments were carried out at 17° C in a glass cylinder standing in a battery jar full of water by means of which its temperature could be regulated; the contents of the cylinder were stirred from time to time by bubbles of carbon dioxide.

Experiment 1. — 20 cc iodide were added to the oxidizing mixture, and then, immediately, 3.05 cc thiosulphate, in one portion: the blue color appeared 932 seconds after adding the iodide.

Experiment 2. — 20 cc iodide were added to the oxidizing mixture, and then 3.85 cc thiosulphate in seven portions, each new portion being added as the blue color reappeared. (See Table II.) The final appearance of the blue color occurred 935 seconds after the addition of the iodide. Thus the rate is not measurably affected by changes in the concentration of the thiosulphate.

Experiment 3. — 20 cc iodide were added to the oxidizing mixture; the amount of iodine liberated in 935 seconds was equivalent to 3.55 cc thiosulphate (instead of 3.85).

Experiment 4. — 3.85 cc thiosulphate were added to the oxidizing mixture and immediately titrated with iodine; 20.35 cc iodine were required.

Experiment 5. — 3.85 cc thiosulphate were added to the oxidizing mixture and an interval of 935 seconds allowed to elapse before titration; 22.33 cc iodine were required. The excess of 10 percent over the reading of Experiment 4 may be referred to formation of sulphite from the thiosulphate under the influence of the acid. The retardation in Experiment 3 is thus most probably due to free iodine.

From these experiments no conclusions can be drawn adverse to the use of the Compensation Method when hydrogen peroxide is the oxidizing agent.

TABLE II.

Under t is entered the time (in seconds from adding the iodide) at which the blue color appeared in the solution; under x the total number of cc thiosulphate that had been added up to that moment; under $A-x$ the residual peroxide; and under k_1 the value of $\log. A/(A-x)$.

t	x	$A-x$	k_1
0	0.0	7.35 **	—
*	0.55	6.8	—
185	1.10	6.25	0.00042
*	1.65	5.7	—
440	2.15	5.2	0.00034
590	4.68	4.67	0.00033
770	3.35	4.0	0.00034
953	3.85	3.5	0.00034

* The watch not read.

** See page 68.

II. CHLORIC ACID AS OXIDIZING AGENT

The experiments of Series B were carried out under the same conditions of temperature and concentration as those of Pendlebury and Seward (see p. 64). The "oxidizing mixture" contained 37.5 grammes of potassium chlorate, 10 cc of a dilute starch solution, and 250 cc of hydrochloric acid (approximately 5 times normal) in a total volume of 900 cc. The temperature was 20° C.

Results of the measurements — Series B

To 900 cc of the oxidizing mixture were added 100 cc one percent potassium iodide solution, and a few drops of a solution of sodium thiosulphate (60 grammes cryst. salt per liter). When the blue color reappeared, the time was noted and 0.5 cc thiosulphate run in from a burette; 215 seconds later the solution again turned blue and another 0.5 cc thiosulphate was added, and so on, as in Table III. The apparatus described on p. 69 was used; a smell of chlorine was perceptible at the mouth of the jar.

TABLE III

A	T	T/A	A	T	T/A
0.5	215	43	0.5	237	475
0.5	215	430	1.5	638	425
0.55	235	428	0.52	233	452
0.52	235	452	0.52	235	452
0.48	222	462	5.0	1567	313
3.0	1120	373	0.5	233	466
0.65	295	347	0.58	267	460
0.5	223	446			

A glance at Table III shows that, with the exception of the first three portions, the time required to destroy 0.5 cc thio-sulphate is constant within the rather large errors of experiment. No correction has therefore been applied to the figures of Table IV for the effect on the rate produced by the addition of sodium salts, or by increase of the volume of the reacting mixture during the experiment.

TABLE IV.

A	T	T/A obs.	T/A calc.
0	—	—	476
0.5	230	460	(460)
1.5	638	425	427
3.0	1120	373	378
5.0	1567	313	(313)

It is apparent that quotient T/A is not independent of A . In Table IV in which the experimental numbers are compared with those calculated from the formula $T/A = 476 - 32.7 A$ shows that, in accordance with equation (4) p. 68, the relation between T/A and A is linear. The amount of thiosulphate in each "small portion" of Pendlebury and Seward's measurements was equal to about 0.5 cc of my solution; hence, by extrapolation, their rates are about 3 percent too high.

As calculated by equation (4) from the data of Table IV,

the value of the rate constant for the direct oxidation of sodium thiosulphate by chloric acid is $k_1 = 0.0003$. An attempt was made to determine its value directly. To 900 cc of the oxidizing mixture were added 100 cc of water, and then 5 cc thio-sulphate. After an interval of one minute, a titration with iodine showed that over 97 percent of the thiosulphate had been oxidized; and after four minutes over 99 percent. The first value corresponds to $k_1 = 3.50$ (instead of 0.0003). Thus the oxidation of thiosulphate by chloric acid is greatly retarded by addition of potassium iodide, and the assumption on which the calculations p. 66 and those of Schükarew are based, viz., that the two reactions, oxidation of iodide, and oxidation of thiosulphate, proceed independently of one another in the same solution, is radically false. It is, in fact, this very retardation that renders the Compensation Method in its original form even approximately applicable with chloric acid as oxidizing agent.

Series C

When discussing Table IV it was pointed out that the rates obtained by the use of the Compensation Method were probably 3 percent too high. This conclusion, based on an extrapolation of a formula which in the light of the experiments of Series B, can only be regarded as purely empirical, is much too favorable to the method in question. Table V, for which I am indebted to Mr. W. C. Bray, shows how widely the results obtained by the Compensation Method may vary from the truth.

TABLE V.

p	500 k_1 (Tit'n.)	500 k_1 (Comp.)
$\frac{1}{16}$	0.172	0.085
$\frac{1}{8}$	0.125	0.10
1	0.12	0.112
3	0.25	0.285
5	0.375	0.43

The experiments were carried out at 30.5° with solutions containing $1/12 \times 122.5$ gm KClO_3 , 1.023×36.4 gm HCl , and $0.0965 p$ gm KI per liter. The numbers entered under

" k_i (tit'n)" were obtained as described below, those under " k_i (comp)" by the Compensation Method.

Not only do the two series differ (in one case by 100 per cent), but while the titration method shows the existence of a minimum rate when $p = 1$, according to the Compensation Method the rate increases continuously with increase in the concentration of the potassium iodide.

Series D — Rate of oxidation of the thiosulphate

A number of experiments were carried out with the object of determining how the rate of oxidation of sodium thiosulphate by chloric acid is affected by changing the concentrations of the reagents involved. As these measurements have only an indirect bearing on the subject of this paper, the results are communicated in as brief a form as possible.

Stock solutions were made up as follows:—

Chlorate: 40.5 grammes KClO_3 in one liter.

Acid: Hydrochloric acid, approximately 4 times normal.

Thiosulphate: 24.8 grammes $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in one liter.

Iodine: 1.28 grammes iodine dissolved (with potassium iodide) in one liter.

In carrying out the measurements, the thiosulphate, chlorate and water, previously brought to the proper temperature, were mixed in a beaker supported in the thermostat; the acid was then added from a pipette, and the time noted. At intervals a portion was removed in a pipette, run into a measured quantity of the "restrainer", and titrated with solutions of iodine and thiosulphate. The "restrainer" consisted of a solution of sodium acetate to which enough sodium bicarbonate had been added to almost neutralize the acid in the portion taken for analysis. Blank experiments showed that the reaction was brought to a standstill without the titer being affected.

Influence of the Thiosulphate.—In the experiments of Table VI where the concentration of the thiosulphate is much less than those of the other reagents, the "constant of the first order", $k_i = (1/t) \log \{ A/(A - x) \}$, is fairly constant when the thio-

sulphate is present in concentration of F/400 or less,¹ while above F/200 the "constant of the second order" is less changeable.

Chlorate; Acid.—On doubling the concentration of the chlorate in experiment *c* of Table VI, the rate is multiplied by less than 1.5; and on doubling the concentration of the acid, the rate is slightly more than doubled.

TABLE VI.

Chlorate, 5 cc; Acid, 5 cc; Total volume, 20 cc; Temperature, 20° C.

Ex.	Thio.	<i>t</i>	A - <i>x</i>	<i>k</i> ₁	<i>k</i> ₂
<i>a</i>	3 cc	0	28.85	—	—
		4	11.83	0.0967	0.0129
<i>b</i>	2 cc	0	19.20	—	—
		4	10.24	0.0885	0.0114
<i>c</i>	1 cc	0	9.65	—	—
		2	7.93	0.0426	0.0117
		4	6.75	0.0421	0.0110
		6	5.46	0.0413	0.0113
<i>d</i>	0.5 cc	0	4.85	—	—
		2	4.20	0.0312	0.0159
		4	3.70	0.0294	0.0160
		6	3.25	0.0289	0.0169
<i>e</i>	0.25 cc	0	2.45	—	—
		2	2.10	0.0335	0.0390
		4	1.80	0.0335	0.0368
		6	1.68	0.0273	0.0312

TABLE VII.

Temperature, 30° C; Total volume, 20 cc; Time, 2 minutes.

Chlorate	Thio.	Sulphite	Acid	Iodine
5 cc	1 cc	0 cc	5 cc	0.84 cc
5	1	1	5	0.06
5	0	1	5	0.00

Sulphite.—A solution of sodium sulphite was prepared containing 31.5 grammes of the crystallized salt per liter. In Table VII the first four columns give the initial composition of the solu-

¹ One four-hundredth of a Formula weight in grammes per liter.

tions, and under "Iodine" is entered the volume of an iodine solution required to produce a blue color with starch at the expiration of two minutes after adding the thiosulphate. (1 cc. Iodine = 1 cc stock thio. = 0.5 cc sulphite.) The acceleration produced by the sulphite is very marked.

III. CHROMIC ACID AS OXIDIZING AGENT

Series E

The experiments of Series E are analogous to those of Series B; and the results are presented in Table VIII, the arrangement being the same as that of Table III.

The oxidizing mixture was made up as follows:—Potassium iodide, 2 grams; potassium bichromate, 0.5 gram; sulphuric acid, 25 cc of 0.975 normal acid; water to make one liter; temperature, 20° C. The solution of sodium thiosulphate in the burette was approximately decinormal.

TABLE VIII.

Ex.	A	T	T/A	Ex.	A	T	T/A
<i>a</i>	0.5	135	270	<i>h</i>	0.48	172	358
<i>b</i>	0.48	145	302	<i>j</i>	0.47 ¹	198	421
<i>c</i>	0.52	148	285	<i>k</i>	0.83 ¹	372	447
<i>d</i>	1.0	280	280	<i>l</i>	0.52	192	369
<i>e</i>	0.5	146	292	<i>m</i>	1.60 ¹	698	436
<i>f</i>	0.5	154	308	<i>n</i>	0.52	201	386
<i>g</i>	3.0	630	210	<i>p</i>	0.5	204	443

Although the time required to oxidize 0.5 cc thiosulphate increases steadily from the beginning to the end of the experiment, it is nevertheless quite obvious that the "oxidation of hydriodic acid" takes place more quickly in the presence than in the absence of thiosulphate (cf. Ex. *j*, *k*, *m*, with Ex. *h*, *l*, and *n*). That the difference is not due to retardation by free iodine, is shown by the similarity of the rates in Ex. *j*, *k*, and *m*, where thiosulphate is absent; it must therefore be ascribed to accelera-

¹ In these three cases the thiosulphate was added *after* the expiration of the *T* seconds.

tion by the thiosulphate, or, more probably, to direct oxidation of the latter. This view is confirmed by a comparison of Ex. *d* and *g* with Ex. *c*, *e*, *f*, and *h*, which shows that increase in the concentration of the thiosulphate increases the rate.

The rate of oxidation of hydrogen iodide by chromic acid, as measured by the Compensation Method, is therefore not unaffected by the presence of the "compensator."

Series F — Influence of potassium iodide on the rate of oxidation of sodium thiosulphate by chromic acid

On p. 72 it has been shown that addition of potassium iodide retards the rate of oxidation of sodium thiosulphate by chloric acid, the experiments of the present series prove that the same effect is produced when chromic acid is the oxidizing agent.¹ The measurements were carried out as described on p. 73; in the presence of much chromate, it was difficult to be sure of the end point of the titration. When the liquid to be analyzed contained free iodine, the restrainer was made up without bicarbonate.

The stock solutions were: Sodium thiosulphate, F/100; potassium bichromate, F/50; sulphuric acid, F/100; potassium iodide, F/10. In Tables X–XIII, $A - x$ gives the number of cc of 0.012-N iodine equivalent to the thiosulphate remaining at time θ ; in the other tables of this series, x represents the number of cc N/100 thiosulphate that have been converted into tetrathionate.

TABLE IX.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C; Time, 3 minutes.

Iodide	0	1	2	3	4	6	8	10	15	30 cc
x	4.65	3.05	2.10	1.25	1.10	0.70	0.85	0.65	0.85	1.55

¹ Likewise with bromic acid. In a mixture containing 10 cc F/100 thiosulphate and 20 cc bromic acid (F/100 KBrO₃ and F/200 H₂SO₄) in 60 cc, 8.4 cc of the thiosulphate were oxidized in 3 minutes at 30° C. If 10 cc of the water were replaced by 10 cc F/10 KI, 7.25 cc were oxidized. When 10 cc iodide and 20 cc bromic acid were diluted to 60 cc, the iodine liberated in 3 minutes was equivalent to 0.2 cc thiosulphate.

Table IX gives the amount of thiosulphate oxidized in three minutes in solutions containing various amounts of potassium iodide; as the quantity of the iodide increases, x first falls, then remains stationary, and finally rises again.

TABLE X.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C.

θ	0	1	2.5	4.5	6.5	9.0	11.5	14.25	16.25	21.0
A - x	8.35	6.6	4.95	4.0	3.5	3.0	2.6	2.4	2.3	2.25

TABLE XI.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Iodide, 4 cc; Vol., 60 cc; Temp., 30° C.

θ	0	1.5	3.5	8	14	20.5	28	35	42.5	68
A - x	8.35	7.9	6.6	5.75	4.6	4.0	3.05	2.55	2.25	1.5

TABLE XII.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Iodide, 8 cc; Vol., 60 cc; Temp., 30° C.

θ	0	2	5	10.5	18	27	34.5	44.5	56
A - x	8.35	7.85	7.05	6.0	5.1	4.35	3.7	2.9	2.75

TABLE XIII.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Iodide, 12 cc; Vol., 60 cc; Temp., 30° C.

θ	0	1.5	5.5	10	18	28	38	48	58
A - x	8.35	7.9	6.65	5.8	4.45	3.55	3.1	2.65	2.2

Tables X, XI, XII and XIII, in which the progress of the

reaction in presence of various amounts of iodide is detailed, establish the existence of a minimum rate when about eight molecules of iodide are added for one of thiosulphate. See Fig. 1.

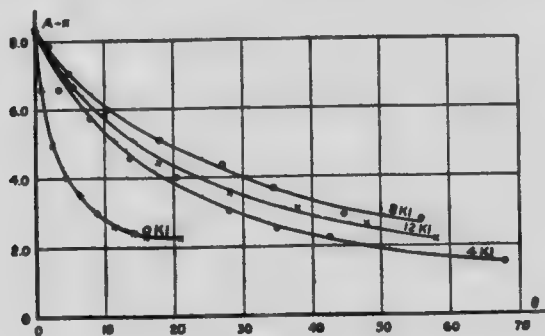


Fig. 1

TABLE XIV.

Thio., 10 cc; Bichr., 5 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C; Time, 5 min.

Iodide	0	2	4	6	8	10	15	20	(40) ¹	(80) cc
<i>x</i>	5.5	3.55	2.05	1.75	1.5	1.45	1.45	1.65	2.35	4.6

TABLE XV.

Thio., 10 cc; Bichr., 2.5 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C; Time, 5 min.

Iodide	0	2	4	8	10	15	(40) cc
<i>x</i>	5.97	4.3	3.21	3.1	3.05	3.1	4.15

Tables XIV and XV show that the amount of iodide present at the minimum is not sensibly changed when the concentration of the bichromate or the duration of the oxidation is

¹ In order to keep the total volume down to 60 cc, an equivalent amount of a more concentrated iodide solution was employed.

varied; while if the concentration of the thiosulphate be halved, the amount of iodide changes from 8 or 10 cc to 2 cc. (Table XVI). The results are represented graphically in Fig. 2.

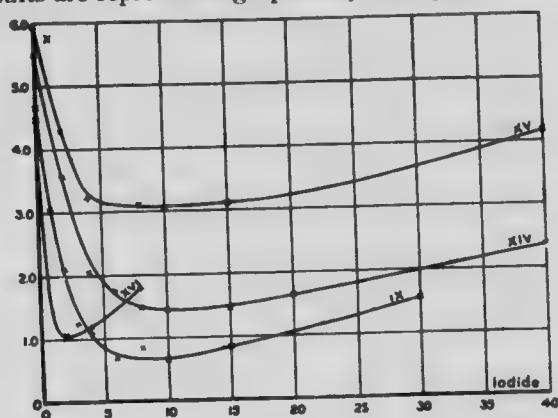


Fig. 2

TABLE XVI.

Thio., 5 cc; Bichr., 10 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C; Time, 3 min.

Iodide	0	2	4	8 cc
<i>x</i>	4.5	1.05	1.2	1.8

TABLE XVII.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C.; Time, 2 min.

Salt added.	<i>x</i>
none	3.95
20 cc F/20 KCl	3.5
20 cc F/20 K ₂ SO ₄	2.5
20 cc F/20 KI	0.6

TABLE XVIII.

Thio., 10 cc; Bichr., 10 cc; Acid, 10 cc; Vol., 60 cc; Temp., 30° C.; Time, 3 min.

Bromide	0	2	5	10	20	(100)	(200) cc
<i>x</i>	4.65	4.4	4.25	4.15	4.05	3.4	3.1

Experiments with potassium sulphate and chloride (Table XVII) show that these salts also retard the rate, but to a much less extent than the iodide. A series of experiments was carried out with F/10 potassium bromide (Table XVIII), but no minimum was observed.

A plausible explanation of the form of the curves in Fig. 2 is afforded by the supposition, that of the two reactions (direct oxidation of the thiosulphate and oxidation of the iodide) the former is retarded by the addition of iodide, while the rate of the second is proportional to the concentration of the iodide.

I hoped to be able to test this hypothesis by analyzing the reaction product corresponding to different points on the curve. Unfortunately for this purpose, the substance formed is always the same, viz., sodium tetrathionate, whether the oxidizing agent be iodine, chromic acid, or a mixture of the two.¹

My attempts to reach a satisfactory explanation of the retardation itself, likewise led to ambiguous results. As the oxidation is retarded by potassium iodide, whether the oxidizing agent be chloric, chromic, or bromic acid, and as the amount of iodide that must be added to obtain a minimum rate depends upon the concentration of the thiosulphate, and not upon that of the oxidizing agent, it is natural to suppose that some complex compound of iodide and thiosulphate is formed, which reduces the concentration of the latter, and consequently the rate at which it is oxidized. The existence of crystallized compounds of thiosulphates and iodides lends support to this view. A number of freezing-point and conductivity determinations, however, gave negative results; moreover, the time elapsing before the

¹ The absence of *tri-* and *penta-thionic acids* was proved by qualitative tests with copper salts; *sulphurous acid* is instantaneously oxidized by chromic acid of the strength used in my experiments; a series of experiments in which hydrochloric acid was substituted for sulphuric showed the absence of *sulphuric acid* in the oxidation product; and finally the presence of *tetrathionic acid* in quantity equivalent to the thiosulphate oxidized was established by boiling with silver nitrate, dissolving the silver chromate and iodide with potassium cyanide, and reducing the residual silver sulphide in hydrogen. Details of the method and test analyses will be published elsewhere.

appearance of a precipitate of sulphur in acid solutions of sodium thiosulphate was found to be unaffected by the addition of potassium iodide, whereas von Oettingen has shown that the interval in question depends on the concentration of the thio-sulphate. For the present, therefore, the explanation suggested lacks confirmation.

Series G — Rate of oxidation of thiosulphate by chromic acid

In conclusion I append a few measurements of the rate of oxidation of sodium thiosulphate by chromic acid. In Tables XIX-XXII the initial composition of the reacting mixture is

TABLE XIX.

Thio., F/1200; Bichr., 2F/1200; Acid, 7F/1200; Temp., 0° C.

	A - x	k
0	10.0	—
1.25	9.55	16
5	7.8	22
8.5	6.05	26
12.5	4.75	26
17.5	3.73	25
26.5	2.65	22

TABLE XX.

Thio., F/1200; Bichr., 4F/1200; Acid, 7F/1200; Temp., 0° C.

θ	A - x	k
0	10.0	—
1.0	9.54	21
3.75	3.45	20
7.5	7.48	17
12.5	5.34	22
20.0	3.72	22
27.5	2.88	20
35.0	2.27	18

TABLE XXI.

Thio., F/1200; Bichr., 2F/1200; Acid, 14F/1200; Temp., 0° C.

θ	$A-x$	k
0	10.0	—
1.08	9.3	29
4	7.45	32
9	5.34	30
15	3.25	33
21	2.34	30
28	1.74	29
31	1.38	28
38.5	1.08	25

TABLE XXII.

Thio., F/1200; Bichr., 2F/1200; Acid, 28F/1200; Temp., 0° C.

θ	$A-x$	k
0	10.0	—
1	9.24	34
3.5	7.56	35
7.25	5.4	37
11	4.08	35
15.5	2.76	36
22	1.98	32
37	1.08	26

given at the head of each table: "Thio., F/1200," for instance, signifying 1/1200 gramme formula weight per liter. For each analysis 100 cc were taken; the iodine reading is entered under $A-x$, and under θ the duration of the reaction in minutes. The "Acid" used was sulphuric acid.

The constancy of $k_1 = 1000/\theta \cdot \log [A/(A-x)]$ shows that the rate of oxidation is proportional to the concentration of the thiosulphate.

Ferrous sulphate and copper sulphate accelerate the reaction; ferric, nickel, and cobalt salts slightly retard it, while starch, sodium tungstate, and ammonium molybdate are without effect. Direct sunlight exerts a very appreciable accelerating influence.

Doubling the concentration of the bichromate slightly re-

tards the rate (Tables XIX and XXI); doubling that of the acid increases the rate by 20 percent or so (Tables XIX, XXI, and XXII).

Summary

In the *Introduction* the Compensation Method is described, the assumptions on which it is based are analyzed, a number of cases in which it has been employed are detailed, and the consequences of the hypothesis that the oxidation of thiosulphate and of iodide proceed independently in the same solution, are developed (pp. 61-68).

Experiments with *Hydrogen Peroxide* show that with this oxidizing agent the Compensation Method probably gives reliable results (pp. 68-70).

Experiments with *Chloric Acid* show that sodium thiosulphate is rapidly attacked by this substance and that its rate of oxidation is retarded by potassium iodide. Thus the assumptions on which the Compensation Method is based, both in its original form, and as modified on p. 65, are untenable when chloric acid is the oxidizing agent (pp. 70-75).

The retardation itself, however, is obviously a distinct advantage where thiosulphate is employed as a "compensator."

Experiments with *Chromic Acid* (and one with *Bromic Acid*) lead to the same conclusion as those with chloric acid. Closer examination of the retardation produced by potassium iodide resulted in the discovery of a minimum rate; hypotheses have been advanced to account for the minimum, and for the retardation (pp. 75-83).

In addition, the paper contains a number of measurements of the *rate of oxidation of sodium thiosulphate* by chloric and chromic acids, with particular reference to the effect produced by adding catalytic agents, and by changing the concentrations of the thiosulphate, the acid, and the oxidizing agent. The results do not suggest any simple "mechanism" for the reaction.

In conclusion, I wish to express my thanks to Professor W. Lash Miller, at whose suggestion this research was undertaken, and under whose direction it has been carried out.

*The University of Toronto,
July, 1902*